

Ethylene glycol-mediated synthesis of PbO nanocrystal from PbSO₄: A major component of lead paste in spent lead acid battery

Jiakuan Yang^{a,b,*}, Xinfeng Zhu^a, R. Vasant Kumar^b

^a School of Environmental Science and Engineering, Huazhong University of Science and Technology (HUST), Wuhan, Hubei 430074, PR China

^b Department of Materials Science and Metallurgy, University of Cambridge, Cambridge CB2 3QZ, UK

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ABSTRACT

Lead sulfate (PbSO₄) is a major component of lead paste of spent lead acid batteries, normally over 60%. In traditional pyrometallurgical process, the decomposition of PbSO₄ requires a relatively high temperature and the use of coal as both the reducing agent and as the source of thermal energy, thereby causing emissions of SO_x, lead particles and CO₂. In this study, lead sulfate was desulfated by adding an aqueous solution comprising citric acid and tri-sodium citrate with the modulation of ethylene glycol (EG) in order to control the morphology. The treating agent reacted with lead sulfate to form an aqueous solution of sodium sulfate and a precipitated precursor of lead carboxylate crystals. The precursor was characterized by XRD, SEM, SDT and FTIR. The morphology of the EG-mediated precursor showed a regular columnar shape. On calcining at relatively low temperatures, EG-mediated precursor was transformed into fine particles of lead oxide. The characteristics of calcined products were investigated by XRD, SEM, and TEM. The results showed that nanostructured crystals of lead oxide could be easily prepared by combustion of EG-mediated precursor at 350 °C with a lead recovery of about 98%. This paper has paved the way for obtaining nanostructured PbO from waste battery scrap.

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1. Introduction

In recent years, nanostructures have attracted considerable attention because of their unique properties and their potential applications in nanostructured electrodes and functional materials [1–3]. Lead oxides are mostly used as active materials in lead acid batteries. Previous studies have been focused on improving the discharge capacity and cycle life of lead acid batteries using nanostructured lead oxides as the electrode materials [4,5]. Nanobelts [6] of PbO₂ were prepared by evaporating commercial PbO powders at high temperature. Nanorods of PbO₂ and Pb₃O₄ [7] were synthesized by adding cetyltrimethyl ammonium bromide (CTAB) to a Pb(NO₃)₂ solution. Recently Karami et al. [8,9] reported that lead oxide nanoparticles can be synthesized by using sonochemical method, and the resulting lead oxide nanoparticles can be applied in the cathode and the anode of a lead-acid battery.

The lead acid battery with a good discharge capacity and cycle life has been widely applied in automobiles, electric vehicles, and hybrid electric vehicles. The greatest growth area for lead products is in sealed valve-regulated lead acid (VRLA) batteries. The

environmental exposure of a toxic metal has been reduced by extremely high recycling rates of >90% of spent lead acid battery products. Nevertheless, the related environmental impact is still a considerable problem in the traditional pyrometallurgical process for recycling spent lead acid batteries [10]. Dry lead paste from spent lead acid battery consists of over 60 wt% of lead sulfate (PbSO₄), 30–40 wt% of lead oxides and 1–5 wt% metallic lead. In the conventional pyrometallurgical process, the decomposition of PbSO₄ requires a relatively high temperature (>900 °C) and the use of coal or coke as the source of reductant and energy, resulting in the emission of acid gases (SO_x) and greenhouse gas (CO₂) [11]. Lead compounds are highly volatile, so any high temperature process will inevitably result in lead fuming, and emission of lead particulates into the environment.

In recent years, alternative routes of recovering secondary lead using hydrometallurgical process at room temperature have received much interest [12,13]. A novel process of recovering lead has been developed at University of Cambridge [14,15]. In this process, waste lead acid battery paste is treated with aqueous citric acid solution and sodium citrate so as to generate lead carboxylate precursors which are separated from soluble sulfate solutions. Calcination of lead carboxylate precursor at relatively low temperature of 350 °C can generate PbO (with controlled amounts of Pb) which can then be directly used for making new pastes for a battery. The preparation of nanostructured PbO from such precursors is an interesting option.

* Corresponding author at: School of Environmental Science and Engineering, Huazhong University of Science and Technology (HUST), Wuhan, Hubei 430074, PR China. Tel.: +86 27 87792207; fax: +86 27 87792101.

E-mail addresses: jkyang@mail.hust.edu.cn, yjiakuan@hotmail.com (J. Yang).

The Pechini process has been used for the preparation of ultra fine powders of a variety of metal oxides at low calcining temperatures using carboxylic acids and polyhydroxyl alcohols as both fuels and chelating agents [16]. The principle of the Pechini process is based on the ability of carboxylic acids to chelate the metal ions, which can undergo polyesterification with polyhydroxyl alcohols [17]. Nature of polyhydroxyl alcohols is very important for the formation of polymeric intermediates, which can determine the morphology and the resulting physiochemical properties of the oxides. Ethylene glycol is commonly used as a mediator of polyhydroxyl alcohol. Jiang et al. [18] reported ethylene glycol-mediated synthesis of metal oxide nanowires. Chen et al. [19] reported the preparation of Pd nanoparticles using ethylene glycol. Wongkasemjit et al. [20] investigated the electrical properties of a lead glycolate precursor by using lead acetate trihydrate and ethylene glycol as starting materials. Wolcott et al. [21] reported the synthesis and characterization of ultrathin WO_3 nanodisks utilizing long-chain poly(ethylene glycol).

Although several papers have indicated the advantages of using nanocrystalline PbO as the starting material for making pastes for a new lead acid battery [8,9], this is the first report of directly converting PbSO_4 (the majority component in a spent battery which is also relatively the most difficult component to leach out and/or to decompose) into nanocrystals of PbO with controlled morphology using the mediating effect of ethylene glycol. Mediation with ethylene glycol is used to improve the resulting morphology of both the lead citrate precursor and the resulting PbO after combustion–calcination.

2. Experimental

2.1. Chemical agents

Lead sulfate (PbSO_4 , >99% purity) was simulated as a major component in the waste lead acid battery scrap. Citric acid (CA) monohydrate ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$, 99.5% purity) was dissolved in distilled water and used for the leaching–crystallization step. Tri-sodium citrate hydrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$, >99% purity) was used as a desulfating agent for PbSO_4 . Analytical grade ethylene glycol (EG) was used as a mediator. All chemicals were purchased from Fisher Scientific Company, and were used as received without any further treatment.

2.2. Synthesis of lead carboxylate precursors

5 g of lead sulfate powder was added to citric acid and trisodium citrate solution with lead: citric acid: trisodium citrate mol ratio of 1:1:2, and with a solid/liquid (S/L) mass ratio of 1:5. Trisodium citrate contributed to desulfurization by reacting with lead sulfate to form soluble sodium sulfate. Effect of EG on the process was considered by adding 13.9 g of EG to the above solution.

The first leaching process with the aqueous citric acid/sodium citrate solution was carried out under magnetic stirring at a speed of 500 rpm for 1 h at 20 °C. After completion of the reaction, the resulting white precipitate was allowed to settle for 15 min. Then the collected solids were washed with distilled water, filtered and dried at 65 °C for 24 h to obtain the first lead carboxylate precursor, called as CA precursor. The second leaching process using both citric acid/sodium citrate and EG in an aqueous solution was carried out under magnetic stirring at a speed of 500 rpm for 24 h at 20 °C. The white flocculate was harvested using centrifugation, followed by washing with distilled water and ethanol to remove excessive soluble residues from the flocculate. The precipitate was finally dried at 65 °C for 24 h to obtain the second lead carboxylate precursor, called as EG precursor.

After leaching, filtering, and washing procedures, the spent solution was diluted in a 250 ml volumetric flask. The concentration of lead ion in the spent solution was analyzed by ICP-OES Spectrometer (Liberty series II, Varian Australia). The amount of lead in the lead carboxylate precursor was calculated by subtracting the amount of lead in the spent solution from the total amount of lead in the starting materials. The recovery rate of lead was deduced by the ratio of the amount of lead in the lead carboxylate precursor to the amount of lead in the starting material of lead sulfate.

2.3. Characterization of lead carboxylate precursors

Thermal analysis of the precursors was performed in alumina crucibles by SDT (Simultaneous DSC-TGA), carried out by TA Instruments Q600 SDT, with an air flow rate of $100 \text{ cm}^3 \text{ min}^{-1}$, and a heating rate of $10^\circ \text{C min}^{-1}$ in the range from 20 °C to 1400 °C. Morphology of the precursors was investigated with scanning electron microscopy (JEOL 820 SEM, Tokyo, Japan) using gold coated samples. X-ray diffraction (XRD) data were collected from powder samples using a PW1820 Goniometer (Philips, PANalytical B.V. Almelo, the Netherlands) with $\text{Cu K}\alpha$ radiation and $\lambda = 1.54056 \text{ \AA}$ at a scanning rate of $0.005^\circ \text{ s}^{-1}$ for 2θ in the range from 3° to 80°. The FTIR spectra of the precursors were obtained using a Bruker Optics Tensor 27 FTIR.

2.4. Synthesis and characterization of calcined products from EG precursors

The EG precursor powders were calcined at 300 °C, 350 °C, 400 °C, and 450 °C for 1 h in static air. The weight loss was monitored for each set of the experiment. The phases of the as-decomposed samples were identified by powder X-ray diffraction (Philips, PW1820 Goniometer, PANalytical B.V. Almelo, the Netherlands) with $\text{Cu K}\alpha$ radiation, and $\lambda = 1.54056 \text{ \AA}$ at a scanning rate of $0.05^\circ \text{ s}^{-1}$ for 2θ in the range from 10° to 140°. Scanning electron microscopy (SEM) images were investigated with a field-emission microscope (JEOL 6340F FEGSEM) operated at 5 kV after the combustion products samples coated with platinum. Transmission electron microscopy (TEM) images of the EG precursor and its calcined product at 350 °C were collected with JEOL 2000FX operated at 200 kV. Bright field images and selected-area electron diffraction pattern (SAED) images were investigated. Samples for TEM were prepared by placing one drop of diethyl ether suspension on the carbon-coated copper grid, followed by evaporating off the solvent under vacuum.

3. Results and discussion

3.1. Recovery of lead after leaching and crystallization

The mass of solid products of lead carboxylate precursor after filtering and the concentration of lead ion left in the spent solution are summarized in Table 1. As shown in Table 1, the recovery of lead with both CA and EG is comparable at 97.85–98.46%. It is important to ascertain that addition of mediator does not negatively impact the good recovery available from CA.

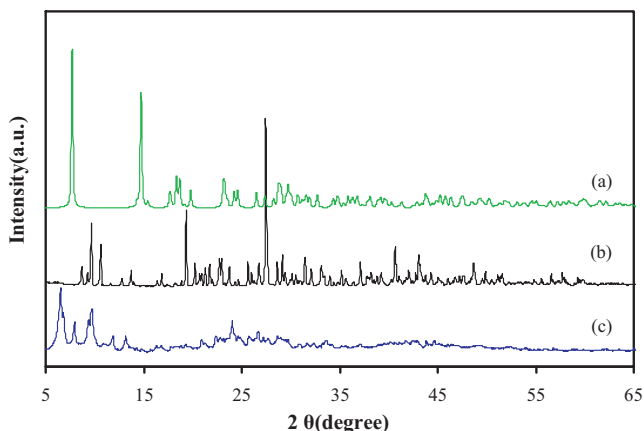
3.2. Crystallization characteristics of the lead carboxylate precursors

The XRD patterns of the two precursors are shown in Fig. 1. The pattern of standard lead citrate is shown in Fig. 1a, taken from the Cambridge Structural Database (CSD). The standard form of lead citrate $[\text{Pb}(\text{C}_6\text{H}_5\text{O}_7)] \cdot \text{H}_2\text{O}$ is produced on reacting dissolved lead salts (such as lead nitrate) [23]. The CA precursor (using citric acid

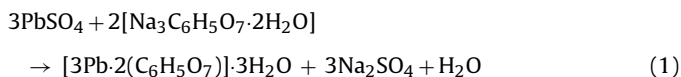
Table 1

The concentration of lead in the spent solution and the recovery of lead.

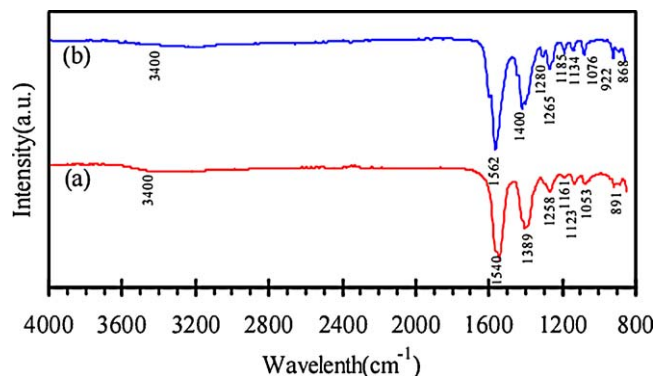
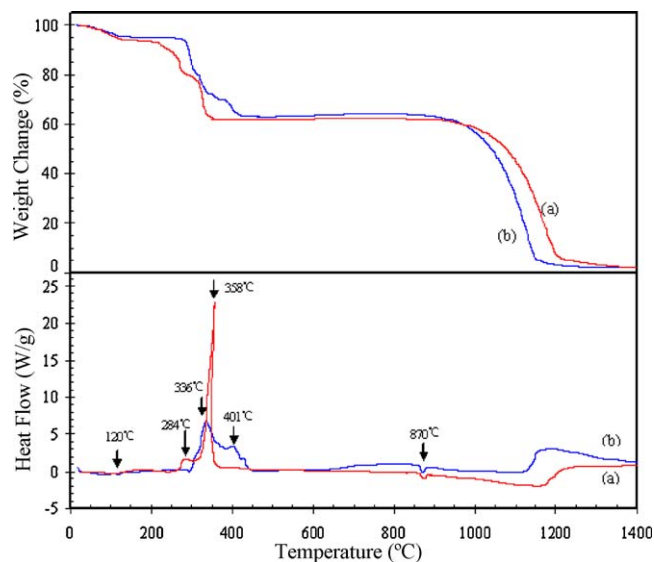
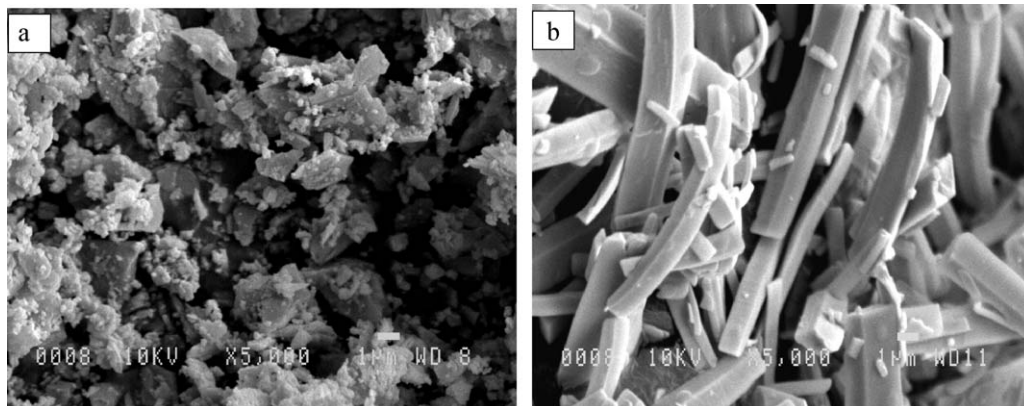
Leaching procedure	Mass of original lead compound (g)	Concentration of lead in the spent solution (mg L ⁻¹) ^a	Recovery of lead (%)
PbSO ₄ + CA ^b	5.000	290.30	97.85
PbSO ₄ + CA + EG ^c	5.000	208.90	98.46

^a Each of leaching solution was diluted in a 250 ml volumetric flask.^b CA refers to citric acid (aq) + sodium citrate (aq).^c CA + EG refers to citric acid (aq) + sodium citrate (aq) + ethylene glycol (aq).**Fig. 1.** XRD patterns of different lead carboxylates: (a) standard lead citrate from CSD, (b) EG precursor, and (c) CA precursor.

and sodium citrate) has already been shown to produce a new citrate composition and structure [15,24]. The chemical reaction for the new citrate composition is given below:



It is known that Pb^{2+} (aq) can change from hard to soft metal ion character and thus can exhibit a multitude of ligand co-ordination modes [20,23,25]. In $[\text{Pb}(\text{C}_6\text{H}_5\text{O}_7)] \cdot \text{H}_2\text{O}$, citrate ions act as doubly deprotonated ligand, co-ordinating to Pb^{2+} forming dimeric units leading to a 2D network, promoting plate formation in crystals. As can be seen, the tricarboxylate citrate ion (as in Na citrate) can change the character of complex formation and a new assembly is promoted (Fig. 1b). Addition of EG, as a mediating component, has led to the formation of another different carboxylate phase (Fig. 1c). The resulting pattern shows no matching with lead glycolate [25]. Reflections for lead sulfate are also not detected, indicating good

**Fig. 3.** FTIR spectra of the CA precursor (a) and the EG precursor (b).**Fig. 4.** DSC/TGA curves of the CA precursor (a) and EG precursor (b).**Fig. 2.** SEM images of the CA precursor (a) and the EG precursor (b).

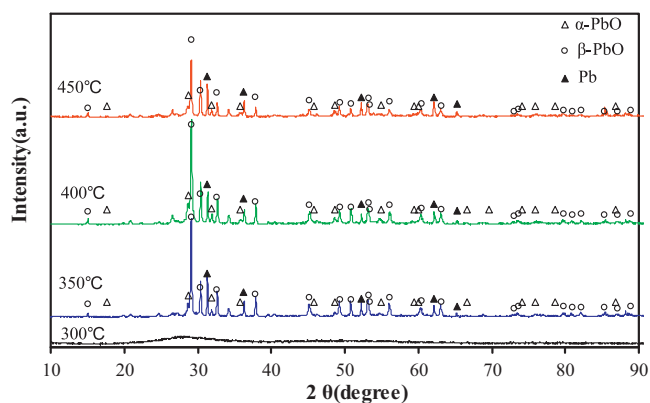


Fig. 5. XRD patterns of calcined products from the EG precursor at different temperatures.

desulfation of lead sulfate. It is reported that glycols can readily serve as ligands and in this situation it is suggested that the glycol has combined with the CA system to form strong complexing with lead from the sulfate.

Fig. 2 shows morphologies of both precursors. Fig. 2a shows that the CA precursors are particles with irregular shape in the size range of 1–10 μm , indicating that the crystallites of organic leaching products grew up non-uniformly in the leaching process, consistent with previous reports [15]. On the other hand, Fig. 2b shows that the EG precursor has regular columnar-like or rectangular rod-like morphology, with rectangular section of

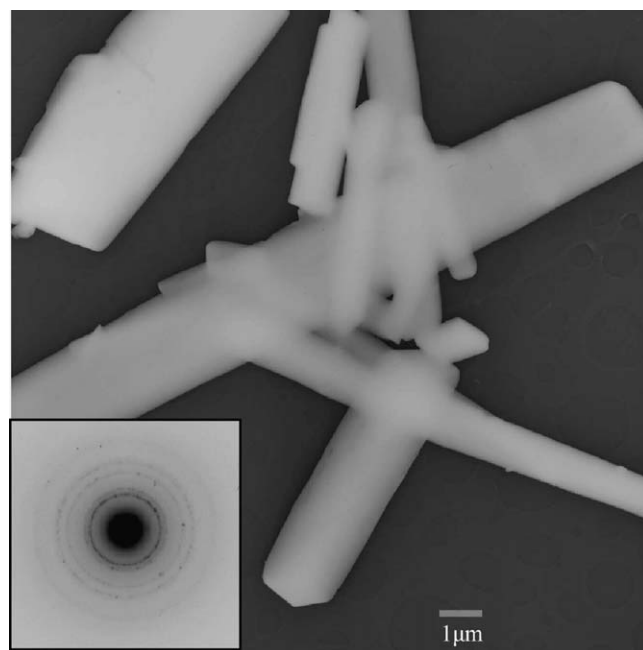


Fig. 7. TEM images of EG precursor. The inset shows the selected-area electron diffraction pattern image of EG precursor.

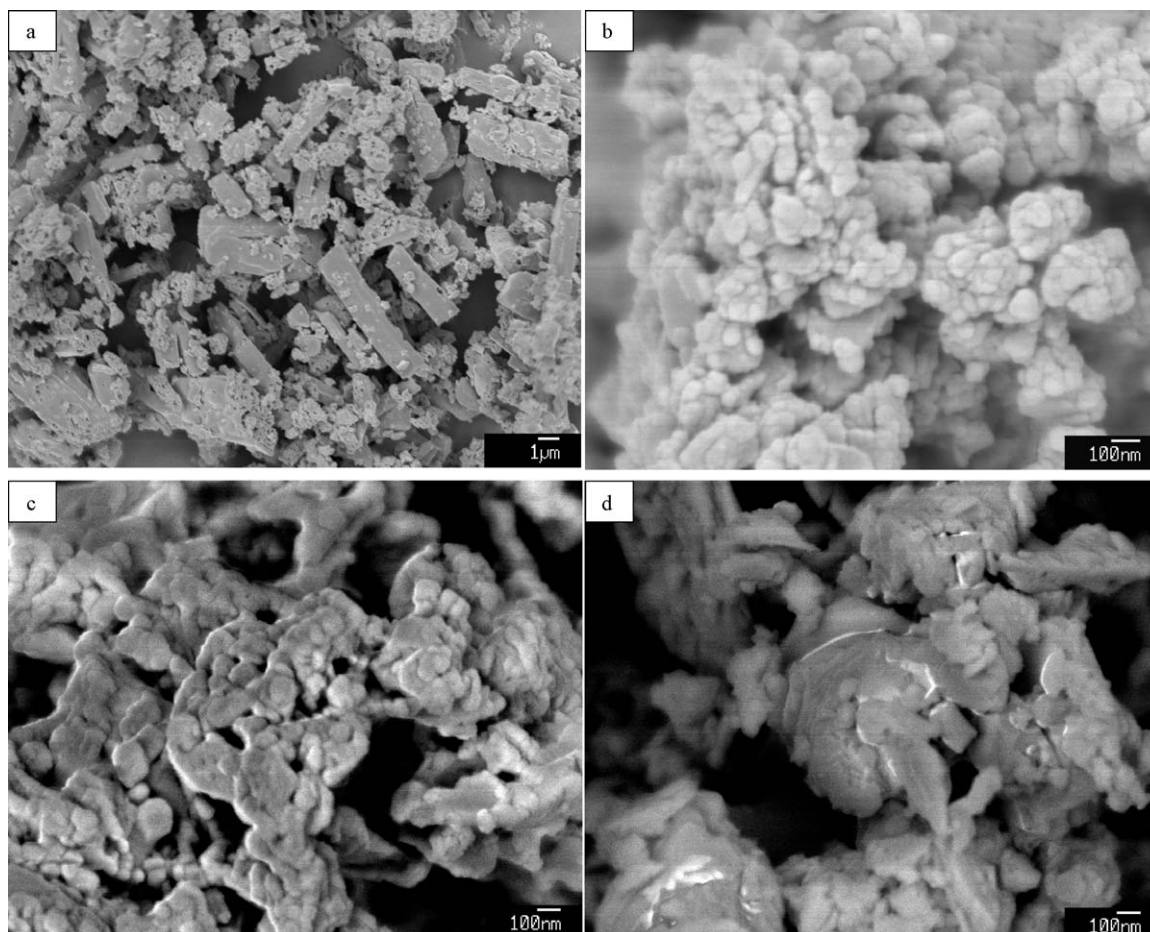


Fig. 6. SEM images of calcined products from the EG precursor at different temperatures: (a) 300 °C, (b) 350 °C, (c) 400 °C, and (d) 450 °C.

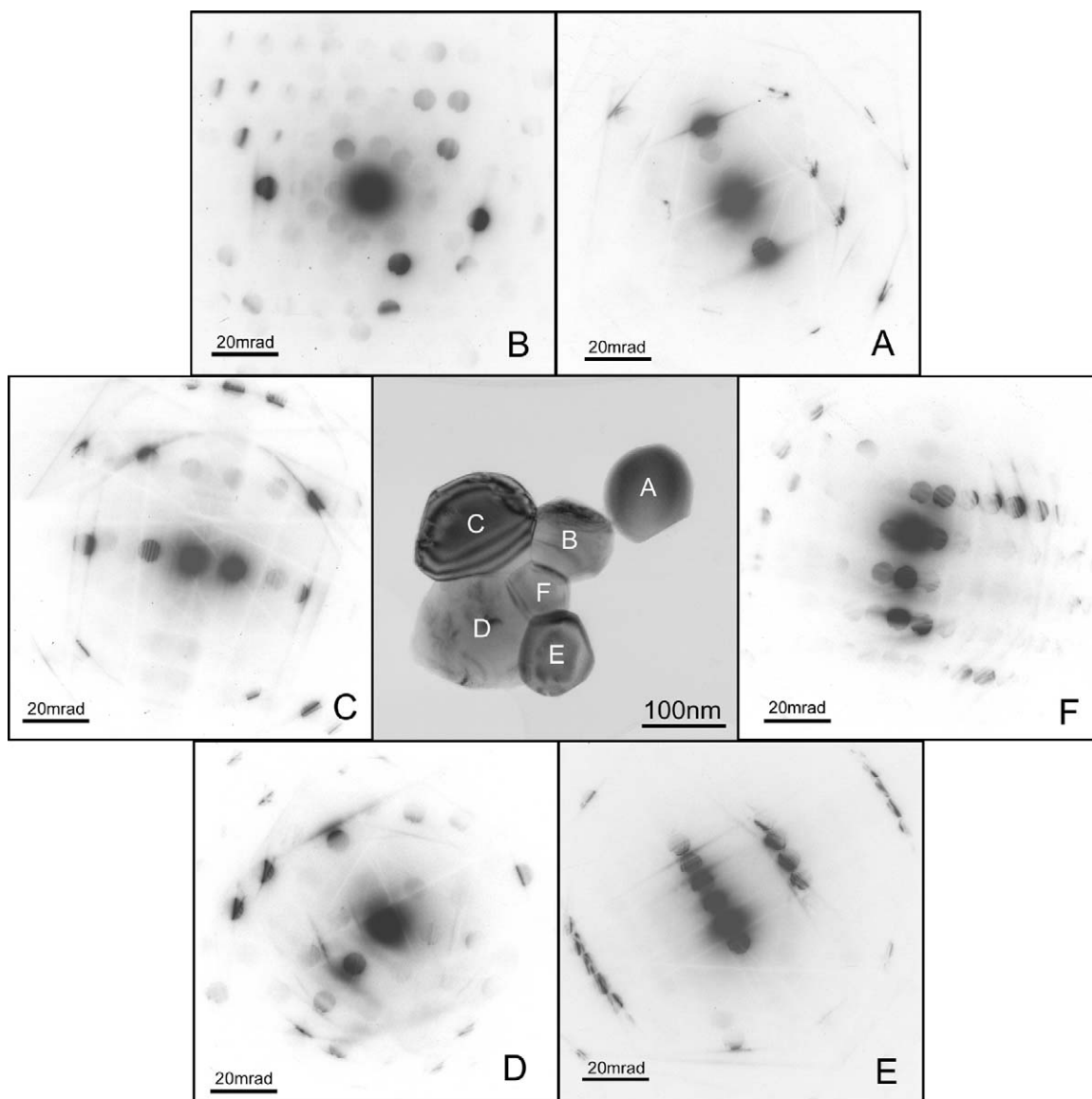


Fig. 8. TEM images of calcined products from the EG precursor at 350 °C: in middle, bright field image; at surroundings, CBED patterns of the different particles of A–F.

about $1\ \mu\text{m} \times 1\ \mu\text{m}$, and with the length of about $10\ \mu\text{m}$. Previous studies have shown that the ethylene glycol can promote the growth of linear polymers by promoting chain-like co-ordination with Pb(II) ions [18]. In this work, we can clearly see the effect of EG on changing the growth mechanism of lead carboxylate by modifying the polymeric structure itself possibly by self-incorporation.

The typical FTIR spectra of different precursors are shown in Fig. 3. The broad peak was observed at about $3400\ \text{cm}^{-1}$ region for both of precursors, which was associated with the O–H stretching vibration, indicating the existence of the hydroxyl bands. Moreover, the bands at $1540\text{--}1565\ \text{cm}^{-1}$ and $1380\text{--}1440\ \text{cm}^{-1}$ for both of precursors were assigned respectively, to the asymmetric and symmetric O–C–O stretching vibration of carboxylate group denoting co-ordination of carboxylate oxygen to Pb(II) [22]. However, the FTIR spectrum of EG precursor showed additional features when compared to that of CA precursor. The stronger band at $1076\ \text{cm}^{-1}$ for EG precursor was attributed to the C–O–Pb stretching of ethylene glycol bidentate ligand as reported in the literature [20]. Moreover, an ester formation between ethylene glycol and citric

acid was confirmed by the C–O stretching band at $1185\ \text{cm}^{-1}$ as reported by Worayingyong et al. [16]. Generally, more peaks were observed in the FTIR spectrum of the EG precursor than that of the CA precursor. The FTIR and the XRD results can be taken to indicate that the structure of the EG precursor might incorporate glycol ligands into the lead citrate promoting linear polymeric structures that can favorably modify the morphology.

3.3. Thermal characteristics of the lead carboxylate precursors

The DSC/TGA curves of the precursors are shown in Fig. 4. The first stage of weight loss of both precursors was observed at about $120\ ^\circ\text{C}$ in the TGA curves, which can be assigned to dehydration reaction, accompanied by an endothermic peak in the DSC curves. During this first stage, the weight loss of both precursors was about 5%. The second stage of weight loss of CA precursor was observed in the range of $170\text{--}360\ ^\circ\text{C}$, accompanied by two exothermic peaks at $284\ ^\circ\text{C}$ and $358\ ^\circ\text{C}$ in the DSC curves, which could be ascribed to combustion decomposition of the carboxylate. The second stage of weight loss of EG precursor could be seen in the

range of 280–450 °C, ascribed to combustion decomposition of the carboxylate, accompanied by two exothermic peaks at 336 °C and 401 °C in the DSC curves. The CA precursor has a lower and a sharper combustion temperature, while the EG precursor has a higher but broader combustion temperature relating possibly to greater stability of polymer chains of the EG precursor. By coincidence, the stoichiometric weight ratio of PbO/hydrocarbon is almost identical at 1.66 in both the lead citrate and the lead glycolate regions of a co-polymer chain, which should give a theoretical wt loss of 37.5% due to combustion to PbO. In the second stage, the weight loss for both of precursors was about 38%, close to the calculated ratio.

At temperatures of higher than 450 °C, both the weight loss and heat flow were constant until about 870 °C which is the melting point of PbO, as shown by an endothermic peak. It indicated that the combustion decomposition of carboxylate matter is completed at 450 °C. Therefore, the subsequent calcination experiments of the precursors for synthesis of PbO were conducted at temperatures lower than 450 °C. Isothermal combustion–calcination of the EG precursor in air showed that 38 wt% loss was achieved at 350 °C after a duration of 60 min. Further increase in temperature (or time) did not lead to any significant increase in weight loss (a small increase of 0.25–0.5 wt% arises from decomposition of some PbO to Pb).

3.4. The XRD patterns of calcined products of EG precursors

The XRD patterns of the calcined products from EG precursors are shown in Fig. 5. The amorphous peak in the XRD pattern at 300 °C can be related amorphous PbO and to the various organic products left in the calcined product at this temperature. The results showed that the organic carboxylates did not decompose completely at temperatures lower than 300 °C. The EG precursors have been converted to a crystalline mixture of tetragonal α -PbO (JCPDS File No. 85-1288), orthorhombic β -PbO (JCPDS File No. 72-0093) and lead metal (JCPDS File No. 04-0686) at 350 °C, 400 °C, or 450 °C after 1 h of combustion–calcination with orthorhombic β -PbO as the main product.

3.5. The SEM images of calcined products of EG precursors

The SEM images of the calcined products from EG precursors are shown in Fig. 6. The SEM images showed the changes of morphologies of the calcined products at different temperatures. As shown in Fig. 6a, the carboxylate rods are still present and a small proportion of decomposition has occurred, however the PbO product is amorphous. The carboxylates have begun to decompose, but did not decompose completely at 300 °C. As shown in Fig. 6b, the morphologies of the calcined products at 350 °C showed crystals in the size of 50–100 nm. When the calcination temperature is increased up to 400 °C or 450 °C, the particles agglomerated and grew larger, as shown in Figs. 6c and d.

3.6. TEM images of EG precursor and its calcined products

TEM images of EG precursors are shown in Fig. 7. In the bright field images, EG precursor appears as columnar-like or a rectangular rod-like morphology with a length of about 10 μ m, which was consistent with the SEM result shown in Fig. 2. The polycrystalline nature is confirmed by the selected-area electron diffraction pattern (shown as the inset in Fig. 7). TEM images of the calcined products at 350 °C from the EG precursor are shown in Fig. 8. The bright field image showed that the calcined products are nanoparticles with a size of 50–100 nm, which is consistent with the SEM image in Fig. 6b. Convergent beam electron diffraction (CBED) patterns of the different particles (A–F) showed that

calcined products comprised the crystal phases of lead oxides and a small amount of lead, which is consistent with the XRD patterns in Fig. 5. It should be noted that a small proportion of metallic Pb in PbO is desirable for making new pastes for battery formation.

4. Conclusions

Lead sulfate of >99% purity was desulfated by adding an aqueous solution comprising citric acid and tri-sodium citrate and further mediated by the addition of ethylene glycol (EG) as a modifier. Two different precursors were compared, called as CA precursor and EG precursor respectively. The XRD pattern of the EG precursor showed a modified XRD structure which suggested that the EG precursor might combine both the citrate and the glycolate ligands in the lead complex. The morphologies of CA precursors were particles with the irregular shape. However, the EG precursor showed regular columnar-like or tubular rod-like morphology, with a crystal length of about 10 μ m.

The EG precursors have been completely converted to a crystalline mixture of tetragonal α -PbO, orthorhombic β -PbO and lead metal at temperatures higher than 350 °C. Morphologies of the calcined products at 350 °C were nanoparticles in the size of 50–100 nm. When the calcination temperature was increased to 400 or 450 °C, the particles agglomerated and grew larger.

This paper has described a novel process for preparing nanostructured active materials of lead oxides by using PbSO₄ as a starting material, which can form the basis for recycling spent lead acid batteries at lower temperatures instead of the traditional pyrometallurgical routes. The application of the nanostructured lead oxides with higher surface areas as a cathode or an anode in lead acid batteries will be investigated in further studies.

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